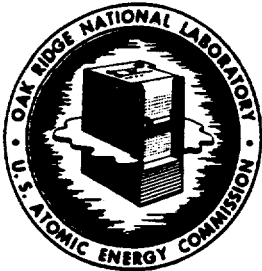


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TABLE OF CONTENTS

	<u>Page</u>
Summary	3
1.0 Introduction	4
2.0 Uranium Metal Reduction	6
2.1 Reduction of $UCl_4$ to Metal and Transfer of Metal to the Amalgam Phase	6
2.2 Observations and Tentative Conclusions	7
2.3 Separation of U Metal from Mercury	10
2.4 Alternate Solvents for $UCl_4$	11
2.5 Electrolysis of $UCl_4$ Solution	11
2.6 Thermodynamics of $UCl_4$ -PDA-Amalgam Reactions	11
3.0 Thorium Metal Reduction	13
3.1 The Preparation of Anhydrous Thorium Chloride	13
3.2 The Preparation of a Thorium Electrolyte Fused Salt	17
3.3 Reduction of Thorium Halides to Metal	19
3.31 The Lithium Amalgam System	19
3.32 Reduction by Electrolysis in a Fused Salt Bath	19
4.0 Production of $UF_4$ from $UO_2F_2$	20
Bibliography	22

TABLE OF FIGURES

Figure 1. The Chloride Route for Uranium and Thorium	5
--	---

TABLES

Table 1. Reduction of $UCl_4$ in Organic Solution with Lithium Amalgam	8,9
Table 2. Dry Chlorination of Thorium Oxide and Thorium Oxalate	15,16
Table 3. Preparation of Thorium Fused Salt Electrolyte	18

## SUMMARY

### Reduction of $\text{UCl}_4$

$\text{UCl}_4$  has been dissolved in propylenediamine and contacted with lithium amalgam at various temperatures, at various concentrations of reactants and in two types of contactors. Uranium metal has been transferred from the PDA- $\text{UCl}_4$  phase to the amalgam phase and subsequently separated from the amalgam.

### Preparation and Reduction of $\text{ThCl}_4$

Anhydrous thorium chloride has been prepared by chlorination of mixtures of thorium oxide and carbon and thorium oxalate and carbon with chlorine and combinations of chlorine and carbon tetrachloride. The mixtures have been leached with dry PDA, to extract the  $\text{ThCl}_4$ . The resulting PDA- $\text{ThCl}_4$  solution has been reduced by Li amalgam, resulting in a transfer of thorium metal to the amalgam phase.

### Electrolytic Reductions

Electrodeposition of thorium from a chloride fused salt bath has been done. An attempt to deposit it in a liquid metal cathode has given only partly satisfactory results. Electrolytic reduction of uranium compounds from aqueous and organic solutions into a lithium amalgam cathode were attempted on a scout-ing scale with no success. One U electrodeposition run was made from a  $\text{UF}_4$ -KCl-LiCl fused salt bath, using molten zinc as a cathode. Considerable metal was deposited at the zinc surface but little penetrated into the main molten zinc body.

### Production of $\text{UF}_4$ from $\text{UO}_2\text{F}_2$

A crystalline double salt was precipitated from a  $\text{UO}_2\text{F}_2$  solution, using a high concentration of ammonium fluoride. This salt was dried and heated in an ammonia and HF atmosphere, reducing it to  $\text{UF}_4$ . The double salt was also heated in a tube furnace with hydrazine hydrate. Good reduction yields were obtained on two of the small scale runs.

## 1.0 INTRODUCTION

A survey of the feed materials preparation program has been undertaken by several agencies to discover, if possible, means of reducing costs. In this study a long range view of the program is taken to determine, if possible, some way of consolidating steps between crude concentrate and metal.

Examination of the costs of the processing steps shows that metal reduction and fabrication are the most expensive. It was reasoned that a continuous method of reducing U compounds to metal would result in some saving. It was also reasoned that a chloride route (Fig.1 ) might offer some opportunity for shortening the overall processing. For this period, effort was directed toward developing and evaluating a method for reducing the chlorides of U and Th, since the chloride route can be of little use unless the reduction step is feasible and economical.

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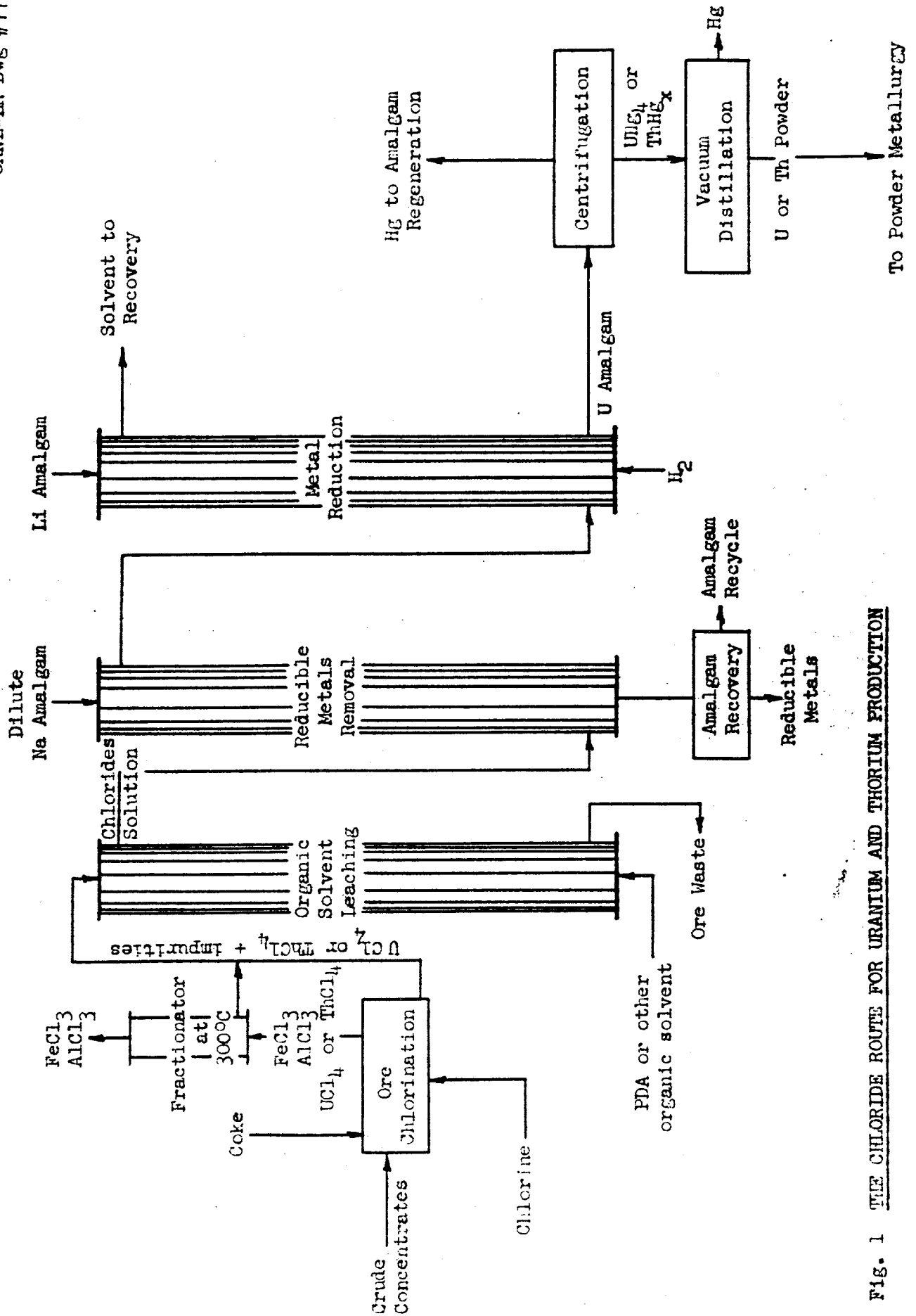


Fig. 1 THE CHLORIDE ROUTE FOR URANIUM AND THORIUM PRODUCTION

## 2.0 URANIUM METAL REDUCTION

### 2.1 Reduction of $\text{UCl}_4$ to Metal and Transfer of Metal to the Amalgam Phase

Thermodynamically, alkali metals, alkaline earth metals and magnesium should reduce halides and oxides of uranium readily.<sup>(1), (2)</sup> In a previous report<sup>(3)</sup> the earlier and more recent efforts to develop reduction methods have been surveyed. In attempting to evaluate a new scheme, three objectives were kept in mind: (a) engineering feasibility; (b) economic advantage over present schemes; (c) making use of reactants and systems whose preparation and function are well known.

Since liquid-liquid contacting systems are well known, it was reasoned that a system based on solutions of uranium and reductant might be attractive. Since  $\text{U}^{\text{IV}}$  compounds hydrolyze readily in water and alkali metals of sufficient potential to reduce U compounds are readily reactive with water, water must be limited to the least practical amount.  $\text{UF}_4$  (more available than  $\text{UCl}_4$ ) would not dissolve or complex with PDA or other common non-aqueous solvents, hence,  $\text{UCl}_4$  was chosen. A few qualitative scouting experiments established:

- (1)  $\text{UCl}_4$  is soluble in or complexed by PDA to the extent of at least 0.567 M
- (2) Concentrations above ~ 0.2 M in U are highly viscous at room temperature.
- (3) Sodium, lithium and potassium amalgams are reactive with  $\text{UCl}_4$ -PDA solutions, forming dark, finely divided solids at the interface.
- (4) If reasonable precautions to keep the water content of the PDA phase below 0.2% were taken, the  $\text{UCl}_4$  and intermediate reduction products appeared to stay in solution or suspension well.
- (5) In spite of precautions to keep the finely divided interfacial solids from contact with atmospheric moisture and oxygen, X-ray diffraction analysis proved these solids to be  $\text{UO}_2$  after they were separated.

One of the test-tube scale experiments in which sodium amalgam was used,

yielded an amalgam phase which tarnished on exposure to air in such a way as to suggest U content. Another in which Li amalgam was used gave stronger indications of the same effect. A repetition of the lithium-amalgam- $\text{UCl}_4$ -PDA contact on a larger scale yielded an amalgam phase from which settled a quasi-solid, which upon analysis proved to U-rich. Analysis of the interfacial solids proved them to be high in U and mercury, but low in chloride.

Efforts to duplicate the above results with sodium amalgams gave only discouraging results. However, results with lithium amalgam could be readily duplicated.

The product from the first 3 attempts to distill mercury away from the quasi-solid amalgam phase was  $\text{UO}_2$ . With greater precaution in elimination of traces of oxygen, however, a small quantity of pyrophoric powder was obtained which was identified by analysis as 95% uranium and 5% mercury.

A more systematic study of the reduction reaction was undertaken to determine optimum U concentrations, PDA water contents, Li concentrations, temperature and extent of U transfer which could be expected in a single contact.

The more significant results of this study are presented in Table 1. The method of contact designated "shaker" involved a glass apparatus, jacketed for temperature control, in which the reactant could be sealed under inert gas and which could be shaken vertically with a slight rotary motion ~60 cycles per minute so that good contact of phases could be achieved. The "Pot" method involved a reflux apparatus in which the interface only was agitated by means of a magnetic stirrer.

## 2.2 Observations and Tentative Conclusions from the Above Series of Experiments

- (1) Lithium amalgam will reduce  $\text{UCl}_4$  to U metal if the  $\text{UCl}_4$  is dispersed in PDA.
- (2) If conditions are optimum, ~75% metal yield may be expected in one equilibrium contact.

Table 1

Reduction of  $UCl_4$  in Organic Solution with Lithium Amalgam

Run No	Reactor Type	Reductant and Volume	$UCl_4$ solution and volume	Temp °C	Contact Time hr	Excess Li %	% of total U transf'd to Hg phase	% of total U remaining in solvent	% of total U in interfacial sludge	Moles Li transf'd per mole U reduced	% of U reduced to metal
5C	Shaker	Li-Hg 0.792 M (51)	0.136 M $UCl_4$ in PDA <sup>4</sup> (21.3)	25	4	243	66.8	23.0	10.2	5.17	77
5D	Shaker	Li-Hg 0.792 M in Li (50)	0.136 M $UCl_4$ in PDA <sup>4</sup> (21.3)	90	4	243	65.8	23.8	10.4	5.22	74.5
6	Pot	Li-Hg 0.792 M in Li (51)	0.087 M $UCl_4$ in PDA <sup>4</sup> (50)	50	5	150	69.0	19.4	6.0	5.54	75
7 <sup>(1)</sup>	Shaker	Li-Hg 0.924 M (40)	0.104 M $UCl_4$ in PDA <sup>4</sup> (50)	50	4	77.3	0.0	96.0	4.0	83	Neg
8 <sup>(1)</sup>	Shaker	Li-Hg 0.875 M (40)	0.104 M $UCl_4$ in PDA <sup>4</sup> (50)	80	4	68	0.0	96.7	3.4	10.0	Neg
9 <sup>(1)</sup>	Shaker	Li-Hg 0.875 M in Li (40)	0.104 M $UCl_4$ in PDA <sup>4</sup> (50)	25	4	68	0.0	96.7	3.4	10.0	Neg
10	Pot	Li-Hg 0.875 M in Li (40)	0.118 M $UCl_4$ in PDA <sup>4</sup> (50)	120	4	48	81	6.3	13.2	4.6	94
11 <sup>(2)</sup>	Shaker	Li-Hg 0.875 M in Li (55)	0.14 M $UCl_4$ in PDA <sup>4</sup> (50)	50	3	42.7	5.2	78.5	10.0	6.3	17



Table 1 (Continued)

Run No	Reactor Type	Reductant and Volume	UCL <sub>4</sub> solution and Volume	Temp °C	Contact Time hr	Excess Li %	% of total U transf'd to Hg phase	% of total U remaining in solvent	% of total U in interfacial sludge	Moles Li transf'd per mole U reduced	% of U reduced to metal
12A	Shaker	0.875 M Li in Hg (25)	0.148 M UCL <sub>4</sub> in PDA <sup>4</sup> (25)	25°	3	55.	54.1	25	20.5	4.4	74.6
12B	Shaker	0.875 M Li in Hg (25)	0.148 M UCL <sub>4</sub> in PDA <sup>4</sup> (25)	50	3	55	71	23.6	5.4	4.1	76.4
12C	Pot	0.875 M Li in Hg (25)	0.148 M UCL <sub>4</sub> in PDA <sup>4</sup> (25)	100	3	55	63.7	31.6	4.9	4.1	67.8
13A	Shaker	0.68 M Li in Hg (50)	0.108 M UCL <sub>4</sub> in IPA <sup>4</sup> (50)	25	3	57	17	80	1.0	15.0	18.0
13B	Shaker	0.68 M Li in Hg (50)	0.108 M UCL <sub>4</sub> in IPA <sup>4</sup> (50)	50	3	57	0.5	97.5	1.5	114	~2.0
13C	Pot	0.68 M Li in Hg (50)	0.108 M UCL <sub>4</sub> in IPA <sup>4</sup> (50)	83	3	57	3.5	44.0	1.2	53	4.7

1. UCL<sub>4</sub> = PDA solution brown-not normal green. PDA had been refluxed over Li-Hg and special precautions used to eliminate water.

2. UCL<sub>4</sub> incompletely dissolved due to poor technique.

Numbers in parentheses in columns 3 and 4 represent phase volumes in ml. IPA = isopropyl alcohol.

- (3) Excess amalgam  $> 50\%$  and higher temperatures favor U transfer to the amalgam phase.
- (4) Within the range of  $25^{\circ}\text{C}$  to  $120^{\circ}\text{C}$  the equilibrium is not greatly affected by temperature.
- (5) The bulk of the reaction takes place almost immediately on good contact of phases. (This is very tentative and not sufficiently supported by evidence)
- (6) Lithium consumption per mole of U reduced reflects side reaction, i.e., isopropyl alcohol reacts more readily with the amalgam than does the  $\text{UCl}_4$ .
- (7) Concentrations of  $\text{UCl}_4$  above  $0.2 \text{ M}$  are too viscous to perform well in a reactor at room temperature up to  $50^{\circ}\text{C}$ .
- (8) Tentatively, on the basis of limited data collected in runs 7, 8 and 9 (Table 1), it may be pointed out that water content of PDA is not optimum below  $0.035\%$ . At water percentages above  $0.2$ , the uranium compound precipitates from the organic phase.

### 2.3 Separation of U Metal from Mercury

Lithium acts as a dispersing and wetting agent for U in mercury. As was indicated above, its presence seems to be necessary in order to transfer U to the amalgam phase. The U metal has little tendency to settle in the amalgam as long as the lithium concentration is appreciable ( $0.1 \text{ M}$  or above). If the amalgam phase is washed with water to reduce the Li concentration, the U metal can be readily concentrated by centrifugation. On the basis of one run, it was concentrated by a factor of 10.

The adhering mercury is best removed by distillation in a partial vacuum, while passing a stream of helium or argon. Spectrographic analysis of the first run showed the product to have a residue of  $5\%$  mercury, indicating that the temperature of distillation was not high enough ( $500^{\circ}\text{C}$ ) or that the distillation was not continued long enough. The quasi-solid amalgam tarnishes

rapidly on exposure to air, hence, should be loaded into the mercury still in a dry-box.

#### 2.4 Alternate Solvents for $\text{UCl}_4$

Good anhydrous solvents for  $\text{UCl}_4$  are: alcohols, aliphatic diamines, 100% TBP, dilutions of TBP in Amsco or diphenyl "hexone," and cyclic ethers. Of these, the lower alcohols and hexone react too rapidly with alkali metal amalgams as well as with  $\text{UCl}_4$  (solvolysis) to be practical for this scheme. TBP solutions in Amsco emulsify badly with lithium amalgam.

#### 2.5 Electrolysis of $\text{UCl}_4$ solutions

Electrolysis of a PDA solution of  $\text{UCl}_4$  over a lithium amalgam cathode failed to deposit any metal in the amalgam phase. The conductivity of the solution was very low, indicating that the nature of the  $\text{UCl}_4$  solution is a molecular complex rather than an ionic one.

Electrolysis of a solution of  $\text{UCl}_4$  in tetrahydrofuran over a Li-Hg cathode also failed to deposit metal. No noticeable current flowed.

Electrolysis of aqueous solutions of  $\text{UO}_2\text{Cl}_2$ ,  $\text{UO}_2(\text{NO}_3)_2$ ,  $\text{UCl}_4$ ,  $\text{U}(\text{SO}_4)_2$  and uranyl carbonate were also tried over lithium amalgam cathodes without success in depositing metal. These electrolyses were carried out at 4 and 5 volts and at a current density of 1 amp per square centimeter.

#### 2.6 Thermodynamics of the $\text{UCl}_4$ -PDA-Amalgam Reactions

Considering the reaction:

(1)  $\text{UCl}_{4(s)} + 4 \text{Li}_{(s)} \rightarrow \text{U}_{(s)} + 4 \text{LiCl}_{(s)}$  if all reactants and products are pure and at standard state,  $\Delta F$  for the reaction at 298°K is -139 k-cal per g mole. In the system discussed above the following reactions must be considered in addition to reaction 1:

- (2)  $\text{UCl}_4 + x \text{ PDA} \rightarrow \text{UCl}_4 (\text{PDA})_x$
- (3)  $\text{LiCl} + 2 \text{ PDA} \rightarrow \text{LiCl} (\text{PDA})_2 \Delta H_{298} = -13.8 \text{ k cal/mole Li}$
- (4)  $\text{Li} + 99 \text{ Hg} \rightarrow \text{Li Hg}_{99} \Delta H_{298} = -19.6 \text{ k cal/mole Li}$
- (5)  $\text{U} + 99 \text{ Hg} \rightarrow \text{U Hg}_{99} \Delta H_{298} = \sim -4 \text{ k cal/mole U}$

Energies of solvation and amalgamation are important factors in the success of reaction No. (1). The solvation energy for reaction (2) is unknown but may be roughly approximated from known data on reaction (3) and the following reactions:

- (6)  $\text{LiCl} + 3\text{H}_2\text{O} \rightarrow \text{LiCl}(\text{H}_2\text{O})_3 \Delta H_{298} = -10.8 \text{ k cal}$
- (7)  $\text{LiCl} + 5\text{NH}_3 \rightarrow \text{LiCl}(\text{NH}_3)_5 \Delta H_{298} = -49.5 \text{ k cal}$
- (8)  $\text{ThCl}_4 + 8\text{H}_2\text{O} \rightarrow \text{ThCl}_4(\text{H}_2\text{O})_8 \Delta H_{298} = -46.4 \text{ k cal}$
- (9)  $\text{ThCl}_4 + 12\text{NH}_3 \rightarrow \text{ThCl}_4(\text{NH}_3)_{12} \Delta H_{298} = -169 \text{ k cal}$
- (10)  $\text{UCl}_4 + 12\text{NH}_3 \rightarrow \text{UCl}_4(\text{NH}_3)_{12} \Delta H_{298} = -183 \text{ k cal}$

Other solvation reactions involving di-valent and trivalent metal chlorides show that at the maximum solvation, the average  $\Delta H/n$  for  $\text{H}_2\text{O}$  is of the order of 5.8 k cal per mole of  $\text{H}_2\text{O}$  and that  $\Delta H/n$  for  $\text{NH}_3$  is  $\sim 14$  k cal/mole  $\text{NH}_3$ .  $\Delta H/n$  for PDA with  $\text{LiCl}$  is  $\sim 7$  k cal/mole PDA or close to median between water and ammonia. If a broad assumption can be made that this holds true for higher valence chlorides, then the solvation energies for  $\text{UCl}_4(\text{PDA})_6$  should be  $\sim 10.5$  k cal/mole PDA, and  $\Delta H_{298}$  for reaction (2) would be  $\sim -63$  k cal. If it is permissible for approximation purposes to add the  $\Delta H$  of solvations of reactions (2)-(5) to the  $\Delta F$  of reaction 1 in order to assess the success chances, to -139 k cal/mole U must be added +82 k cal/mole U for solvation. The net driving force would be -57 k cal/mole U.

Sodium chloride does not form a solvate with PDA, and hence the solvation energy of  $\text{UCl}_4 (\text{PDA})_6$  is not balanced. The net solvation energy for the sodium amalgam reaction is estimated at +137 k cal. The  $\Delta F_{298}$  for the reaction  $4 \text{ Na} + \text{UCl}_4 \rightarrow \text{U} + 4 \text{ NaCl}$  is -140 k cal/mole U. The net driving force would be -3 k cal. This seems to be in agreement with the observed facts, i.e., there is very little reaction between sodium amalgam and  $\text{UCl}_4$ -PDA solution, while the reaction between lithium amalgam and the  $\text{UCl}_4$ -PDA proceeds quite readily.

### 3.0 THORIUM METAL REDUCTION

Because of the need for an increase in thorium metal production attention was focused on possible new and continuous methods of reducing thorium chloride or thorium fluoride to metal.

Since it had been demonstrated that uranium tetrachloride could be reduced to metal in PDA solution by lithium amalgam, transferred to the mercury phase and the metal subsequently separated from the mercury phase, investigation and evaluation of a parallel approach for thorium metal is in progress at present.

The electrolytic reduction of thorium salts in a fused salt electrolyte has been investigated by others<sup>(4), (5), (6)</sup> and it has been demonstrated that a high-purity thorium metal can be deposited on a solid molybdenum cathode. The difficulties of separation of the metal from the melt and reoxidation of the metal occurring in the separations processes contributed to low yield. The practicability of the process is very much in doubt, particularly with respect to making it continuous. Electrolytic reduction of thorium fluoride and thorium chloride in fused salt baths is under investigation by this group. Various molten metals and metal combinations are being tried as cathodes to determine the possibility of depositing thorium into them. Investigation of means of subsequent separation of the cathode metal from thorium is also under way. It is hoped that the liquid metal cathode system may solve the difficulties of separating metal from the bath salts without introducing other difficulties equally great.

#### 3.1 The Preparation of Anhydrous Thorium Chloride

The lithium amalgam method of thorium reduction would require a source of anhydrous thorium chloride, since no other known reducible thorium compound is soluble in an organic phase. Thorium nitrate is soluble in TBP, but side reactions make its reduction by alkali metal amalgams unfeasible.

The Ames Laboratory<sup>(7)</sup> has been investigating the chlorination of thorium oxide in the presence of chlorine and other chlorinating agents, but report somewhat discouraging results especially with respect to purity of product. Purification of  $\text{ThCl}_4$  is possible by sublimation at  $\sim 1000^\circ\text{C}$  in a chlorine atmosphere, but this method is beset by equipment corrosion difficulties and incomplete recoveries.

This group is exploring the possibility that low temperature chlorination of the oxide or oxalate may give a reasonably high yield of the tetrachloride, and that it may be subsequently separated from other reaction products by leaching with an organic solvent (PDA, at present). It has been established that thorium chloride is soluble in PDA to at least 0.2 M in two preliminary leaching runs. Leaching of samples obtained from Laboratory chlorinations of oxide and oxalate appeared to proceed satisfactorily on a qualitative basis, though no numbers are as yet available on material balance and thorium recoveries.

Results of several preliminary low temperature chlorinations of oxide and oxalate are presented in Table 2. Yields are correlated with conditions of chlorination. Tentatively it is indicated that carbon in ratio  $\text{Th/C} = 1/1$  should be present either as  $\text{CCl}_4$  or elemental form, that  $475\text{--}500^\circ\text{C}$  is optimum, that 4 hr contact time is optimum under the conditions of the experiments. The method of contacting solid and gaseous phases is an important variable as indicated by the variation in yield when vertical apparatus was used. The effect of the presence of traces of phosphorus was inconclusive and needs more investigation.

One effort to produce a pure solid anhydrous  $\text{ThCl}_4$  by evaporation of a PDA solution from a leaching run produced a salt which had a  $\text{Cl/Th}$  ratio of 4/1, but also had considerable PDA residue which had not been driven off at  $125^\circ\text{C}$  under a 100 mm vacuum.

Table 2

## Dry Chlorination of Thorium Oxide and Oxalate

Run No	Material Chlorinated	Conditions of Chlorination					Product Quality				
		Cl Time	Cl Temp	Carbon Present	Chlorinating agent	Dehydration	Observations	%Th	%Cl	Cl/Th	% Conversion
A	Th(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> · 2 H <sub>2</sub> O	3 hr	320°C	None	Cl <sub>2</sub> Only	250°C 1-1/2 hr	Powdery product		15.89		42 2
B	Th(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	3 hr	300°C	None	CCl <sub>4</sub> Only	250°C 2 hr	Powdery product		7.15		19 2
C	Th(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	2-1/2 hr	600°C	None	Cl <sub>2</sub> + CCl <sub>4</sub>	300°C 1 hr	Powdery product		21.52		57 2
D	Th(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	3 hr	300°C and 475°C	None	Cl <sub>2</sub> + CCl <sub>4</sub>	None	Powdery product	66.6	25.9	2.55	63.7
E	ThO <sub>2</sub>	4 hr	550°C	Th/C = 1/2	Cl <sub>2</sub> + CCl <sub>4</sub>	250°C 1 hr	Sublimed crystals, some talline product	61.8	31.17	3.36	84.0
F	ThO <sub>2</sub>	4 hr	475°C	None	Cl <sub>2</sub> + CCl <sub>4</sub>	None	Crystals, some sublimation	59.79	31.78	3.47	86.7
G	ThO <sub>2</sub>	4 hr	475°C	Th/C = 1/2	Cl <sub>2</sub> Only	None	10% loss by sublimation crystalline	60.73	28.35	3.06	76.5
H	ThO <sub>2</sub>	4 hr	475°C	None	CCl <sub>4</sub> Only	None	Fine crystals some sublimation	62.28	29.44	3.10	77.5

- Chlorine rate for all runs, 100 ml/min. Chlorine was passed through  $\text{CCl}_4$  at 70°C for all runs where  $\text{CCl}_4$  was used.
- Percent conversion calculated on the basis of 37.9% Cl in  $\text{ThCl}_4$ .

Table 2 (Continued)

Run No.	Material Chlorinated	Conditions of Chlorination					Product Quality				
		Cl Time	Cl Temp	Carbon Present	Chlorinating agent	Dehydration	Observations	%Th	%Cl	Cl/Th Conversion %	
I	Th(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	4 hr	475°C	None	Cl <sub>2</sub> + CCl <sub>4</sub>	None	Product powder, 2" i.d. vertical reactor	78.53	10.69	0.89	22.2
J-1	ThO <sub>2</sub>	3-1/2 hr	420°C	Th/C = 1/2	Cl <sub>2</sub> + CCl <sub>4</sub> + PCl <sub>3</sub>	None	Horizontal Reactor, powder	53.86	23.70	2.88	72.0
J-2	Th(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	3-1/2 hr	420°C	Th/C = 1/1.2	Cl <sub>2</sub> + CCl <sub>4</sub> + PCl <sub>3</sub>	None	Horizontal Reactor, powder	54.17	24.34	2.92	73.0
J-3	Th(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	3-1/2 hr	420°C	None	Cl <sub>2</sub> + CCl <sub>4</sub> + PCl <sub>3</sub>	None	Horizontal Reactor, powder	57.18	22.29	2.55	63.7
K-1	Th(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	4 hr	500°C	None	Cl <sub>2</sub> + CCl <sub>4</sub>	None	Horizontal tube reactor. Powder and small crystals	61.63	29.3	3.10	77.5
K-2	Th(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	4 hr	500°C	Th/C = 1/1.2	Cl <sub>2</sub> + CCl <sub>4</sub>	None	Graphite boat	48.66	27.47	3.65	92.3
K-3	Th(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	4 hr	500°C	Th/C = 1/0.6	Cl <sub>2</sub> + CCl <sub>4</sub>	None	Graphite boat	52.59	28.29	3.52	88.1
L	ThO <sub>2</sub>	5-1/2 hr	550°C	Th/C = 1/1.1	Cl <sub>2</sub> + CCl <sub>4</sub>	None	Horizontal tube, graphite boat, crystals	59.94	27.85	3.04	76

3. PCl<sub>3</sub> was placed in the CCl<sub>4</sub> through which Cl<sub>2</sub> was bubbled.



### 3.2 The Preparation of a Thorium Fused Salt Electrolyte

The objective of this series of experiments was to produce a thorium salt suitable for use as an electrolyte in a fused salt bath. Compounds considered suitable were pure anhydrous thorium chloride, anhydrous thorium fluoride, potassium thorium fluoride (or chloride), sodium thorium fluoride (or chloride), lithium thorium fluoride (or chloride), magnesium thorium fluoride (or chloride) and zinc thorium fluoride (or chloride). The double halides were considered because the lower water of hydration - to anhydrous salt ratio and greater stability to hydrolytic action promised an easier way to produce an anhydrous halide without  $\text{ThO}_2$  contamination. The oxide was found to be insoluble in ordinary fused salt combinations. The approach chosen was - (1) dissolution of a thorium compound other than the nitrate in 12 N HCl; (2) addition of  $\sim 1/1$  molar ratio of  $\text{NH}_4\text{Cl}/\text{Th}$ , a practice found helpful in the prevention of hydrolysis of salts like  $\text{MgCl}_2$  and  $\text{ZnCl}_2$ ; (3) addition of the complexing salt in the proper molar ratio; (4) slow evaporation in air of the solution to a paste of crystals without any dehydration; (5) transfer of crystal paste to a graphite pot, blanketing with dried air or  $\text{N}_2$  and dehydration in an electric furnace at  $300^\circ\text{C}$ ; (6) completion by sublimation of the  $\text{NH}_4\text{Cl}$  at  $500^\circ\text{C}$ .

Thorium compounds found to be appreciably soluble in 12 N HCl at  $70^\circ\text{C}$  were  $\text{ThOCO}_3$  and hydrated thorium oxide, precipitated from nitrate solutions. Oxalate was not sufficiently soluble to permit satisfactory thorium concentration. Nitrate was considered objectionable because of its promotion of oxide formation in the dehydration step. Results of preparations by the above method are presented in Table 3.

Some small scale attempts to directly chlorinate oxalate, oxide and carbonate in a KCl-LiCl eutectic melt resulted in complete failure to cause noticeable dissolution of the thorium compounds.

Table 3

Preparation of Thorium Fused Salt Electrolyte

Product Objective	Initial Thorium Material	Dissolution Procedure	Dissolution Results	Crystallization Procedure	Product Quality				Yield
					Dehydration Procedure	Solub'y in H <sub>2</sub> O	Solub'y in LiCl KCl melt	Cl/Th	App. %
Anh. ThCl <sub>4</sub>	ThCO <sub>3</sub>	Th/HCl = 1/10; HCl = 12 M; Th/NH <sub>4</sub> Cl = 1/1.	Complete dissolution	Evap'n to crystal paste	heat 3 hr at 300°C heat 16 hr at 500°C Air	10%	Very slight	1/2	12
LiThCl <sub>5</sub>	Impure ThCO <sub>3</sub>	Th/LiCl = 1/1; Th/NH <sub>4</sub> Cl = 1/1; Th/HCl = 1/10; 70°C, 5 hr	~ 50% dissolution attributed to impure carbonate	Evap'n to crystal paste	heated to 300°C in graphite crucible	~10%	None observable	not analyzed	<10
NaThCl <sub>5</sub>	ThO <sub>2</sub> ·xH <sub>2</sub> O ppt'd from Th(NO <sub>3</sub> ) <sub>4</sub> soln double pptation	Th/NaCl = 1/1; Th/NH <sub>4</sub> Cl = 1/1.1; Th/HCl = 1/10; 70°C, 5 hr.	Complete dissolution	Evap'n to crystal paste	heated to 250°C in graphite crucible under dry N <sub>2</sub> stream	total	~50%	2/1	50
Anh. ThCl <sub>4</sub>	ThO <sub>2</sub> ·xH <sub>2</sub> O as above	Th/NH <sub>4</sub> Cl = 1/1.1; Th/NH <sub>4</sub> Cl = 1/10; 70°C, 5 hr	Complete dissolution	Evap'n to crystal paste	Digestion in isopropyl alcohol, sat. with anh. HCl, 3 hr. Alcohol taken off in vacuo furnace at 500°C in anh. HCl 2 hr	total	~75%	2.44	61
Anh. ThCl <sub>4</sub>	ThO <sub>2</sub> ·xH <sub>2</sub> O as above	as above	Complete dissolution	Partial evap'n pptation forced by bubbling anh HCl, filtered	Dehydrated in a stream of anh. HCl 2 hr at 150°C Furnaced at 500-600°C 16 hr	~85%	~50%	2/1	50

The preparation of anhydrous thorium fluoride has been well worked out by the Ames group. The wet precipitation of  $\text{ThF}_4 \cdot 2\text{H}_2\text{O}$ , followed by air-drying and dehydration in an HF atmosphere will be followed.

To date, the preparation of  $\text{ThCl}_4$  electrolyte by dry chlorination followed PDA leach and evaporation appears more attractive than does the wet method of preparation of  $\text{ThCl}_4$  or double chloride. The use of single rather than double thorium salts is considered more attractive because the complexing salt presents a build-up problem in a continuous electrolytic bath.

The most attractive supporting electrolytes for the bath appears to be LiCl-KCl in a 40.5/59.5 mole % ratio for the chloride system and 45/55 mole % LiF/KF for the fluoride system, based on melting point and stability. Both  $\text{ThF}_4$  and  $\text{ThCl}_4$  are readily soluble in these baths.

### 3.3 Reduction of Thorium Halides to Metal

#### 3.31 The Lithium Amalgam System

One run has been completed, in which 50 ml of a PDA solution containing 2.25 grams of  $\text{ThCl}_4$  was contacted with 50 ml of 0.7 M LiHg at 100°C for 2-1/2 hr. The reaction proceeded smoothly, a black layer forming at the interface and disappearing when the surface of the mercury was stirred. On separation of the phases, removal of excess lithium from the mercury and centrifugation of the mercury phase, a quasi-solid phase was found at the bottom of the centrifuge tubes. Its similarity to that found when a similar procedure was used with uranium indicates a reduction and transfer of thorium metal to the mercury phase. Until analysis reports are received, only qualitative statements based on visual observations can be made.

#### 3.32 Reduction by Electrolysis in a Fused Salt Bath

Three scouting runs were made, attempting to electrodeposit thorium metal into a molten zinc cathode from a LiCl-KCl- $\text{ThCl}_4$  fused bath. The molten salt mixture overlaid the molten zinc in a graphite crucible. The entire assembly

was kept in an argon atmosphere by means of a pyrex envelope. The graphite crucible was made cathodic, and a graphite anode dipped into the upper portion of the molten salts mixture. Very little thorium metal was deposited into the main body of molten zinc, but some was deposited at the zinc surface, which tended to bridge across to the anode and short-circuit the cell. The deposit was powdery and pyrophoric. There was some small indication that thorium powder was wetted by zinc at the interface, and that stirring the cathode might cause absorption of the thorium into the main zinc body. The  $\text{ThCl}_4$  used was that made in the earlier runs by dry chlorination and wet crystallization methods described above and was of poor quality.

Because the phase diagram for thorium-bismuth indicated greater thorium solubility in bismuth than in zinc, and because it is possible to distill bismuth from a Bi-Th alloy, 2 runs were made using molten Bi as a cathode. Results were similar to those produced with the zinc cathode, with only trace quantities of thorium penetrating to the main cathode mass. One run was made using  $\text{ThF}_4$  in  $\text{LiCl-KCl}$  supporting electrolyte and zinc cathode. Results were similar to those of the previous runs.

#### 4.0 PRODUCTION OF $\text{UF}_4$ FROM $\text{UO}_2\text{F}_2$

Eluate from the Higgins contactor is  $\sim 0.55 \text{ M}$  in  $\text{UO}_2\text{F}_2$  and  $1.35 \text{ M}$   $\text{HF}$ . If equal volumes of this solution and a saturated ammonium fluoride solution are mixed at a pH of 5,  $> 99\%$  of the U is precipitated as a crystalline double salt, corresponding roughly to the formula  $\text{UO}_2\text{F}_2 \cdot \text{HF} \cdot \text{NH}_4\text{F}$ . This salt filters readily and dries quickly at  $160^\circ\text{C}$ . If the double salt is placed in a boat in a nickel reactor and heated in an atmosphere of  $\text{NH}_3 + \text{HF}$ , it is reduced to  $\text{UF}_4$ . The scouting runs made gave  $\sim 50\%$  reduction, but other workers have reported  $> 95\%$  on similar salts.

Two reduction runs, using a 1/8 molar ratio of hydrazine hydrate to uranium gave greater than 95% reduction in a reactor with no ammonia or HF added. The present cost of hydrazine, ~\$3.00 per pound, makes the latter reduction unattractive but it may become important if the price of hydrazine should drop to ~25 cents per pound.

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